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971715

Fundamental Limits on NOx Reduction by Plasma

B. M. Penetrante, M. C. Hsiao, B. T. Merritt, and G. E. Vogtlin
Lawrence Livermore National Laboratory

SAE The Engineering Society For Advancing Mobility Land Sea Air and Space.
INTERNATIONAL

International Spring Fuels
& Lubricants Meeting
Dearborn, Michigan
May 5-8, 1997

400 Commonwealth Drive, Warrendale, PA 15096-0001 U.S.A. Tel: (412)776-4841 Fax:(412)776-5760

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1997	Technical Report, May 5-8, 1997

4. TITLE AND SUBTITLE
Fundamental Limits on NOx Reduction by Plasma

5. FUNDING NUMBERS
N/A

6. AUTHOR(S)
B.M. Penetrante, M.C. Hsiao, B.T. Merritt, and G.E. Vogtlin

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Lawrence Livermore National Laboratory

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
SERDP
901 North Stuart St. Suite 303
Arlington, VA 22203

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
N/A

11. SUPPLEMENTARY NOTES

SAE Technical Paper Series, 971715. International Spring Fuels & Lubricants Meeting Dearborn, Michigan, May 5-8, 1997.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release: distribution is unlimited.

12b. DISTRIBUTION CODE
A

13. ABSTRACT ***(Maximum 200 Words)***

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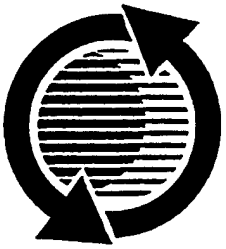
14. SUBJECT TERMS
SERDP, SERDP Collection, NOx reduction, plasma, dissociation energy limit

15. NUMBER OF PAGES
4

16. PRICE CODE
N/A

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclass	unclass	unclass	UL



ISSN 0148-7191

Printed in USA

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B. M. Penetrante, M. C. Hsiao, B. T. Merritt, and G. E. Vogtlin
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ABSTRACT

This paper discusses the gas-phase reaction mechanisms for removal of NO_X in a plasma. The effect of oxygen content on the competition between the reduction and oxidation processes is discussed. The effect of the electron kinetic energy distribution on the radical production and subsequent chemistry is then discussed in order to predict the best performance that can be achieved for NO_X reduction using the plasma alone. The fundamental limit on the minimum electrical energy consumption that will be required to implement NO_X reduction in any type of plasma reactor is established.

INTRODUCTION

Plasma-based methods for the abatement of NO_X in gas streams are being investigated in a number of laboratories [Ref. 1]. One critical issue in the use of plasmas is the electrical energy consumption. For applications to trucks and cars, another critical issue is whether the plasma is removing NO_X by chemical reduction to benign gases.

Plasma processing requires electrical energy. There are many ideas being proposed in an attempt to minimize the electrical energy consumption, including (a) optimization of the electrode structure of the plasma reactor, (b) optimization of the voltage waveform applied to the plasma reactor, and (c) taking advantage of heterogeneous reactions.

It has been difficult to assess and compare the performance of various kinds of plasma reactors. The data presented in the literature using different kinds of reactors often were measured under different gas conditions. In many cases, the data are presented in a way that makes it impossible for the reader to determine the energy consumption of the reactor.

There is also some controversy on what type of efficiency should be improved. There are two kinds of efficiencies that concern the plasma processing community: (a) electrical conversion efficiency, and (b) chemical processing efficiency. The electrical conversion efficiency refers to the efficiency for converting wall plug electrical power into power deposited by the electrons into the plasma. The chemical processing efficiency refers to the amount of pollutant removed or decomposed for a given amount of energy deposited into the plasma. The latter is often expressed in terms of the specific energy consumption in units such as electron volts (eV) per molecule of NO_X, or grams of NO_X per kW-hr. Obviously, if the fundamental limit on the chemical processing efficiency cannot satisfy user requirements, then the development of a 100% electrically efficient reactor will never satisfy those requirements.

Much work has been done in the application of non-thermal plasma methods to the treatment of flue gases from power plants [Ref. 2]. It should be noted, however, that in power plant flue gas treatment applications, the purpose of the plasma is to oxidize NO to NO_2, and eventually to nitric acid. The desired products, in the form of ammonium salts, are then obtained by mixing ammonia with the formed acids. Some form of scrubbing is required to collect the final products.

For applications to the treatment of exhausts from cars and trucks, it is very important to make a distinction between NO removal by chemical oxidation and NO removal by chemical reduction. To avoid the need for scrubbing of process products, the desired method of NO removal is by chemical reduction; i.e. the conversion of NO to benign gaseous products like N_2 and O_2. In the plasma processing literature, many authors carelessly use the term "NO reduction" even when the "NO removal" is accomplished by oxidation to NO_2 and nitric acid.

Heterogeneous reactions in the plasma reactor can also take place in oxidative and reductive modes. Enhanced absorption of NO_2 and nitric acid to

particulates and reactor walls can often be mistaken for chemical reduction. In power plant flue gas treatment applications, there is an abundance of aerosol particles resulting from the plasma oxidation. These aerosols can either enhance the scrubbing of other oxidation products or promote the oxidation process itself. It is very important to establish if the heterogeneous reactions are oxidative or reductive. This can be accomplished through diligent control of operating conditions and careful analysis of process products. However, such basic experiments are best done first under well-controlled simulated conditions rather than actual engine exhaust conditions.

This paper deals with the gaseous phase reactions in the plasma. The main objective is to establish the fundamental limit on the minimum electrical energy consumption that will be required to implement NO_x reduction by the plasma alone. The effect of background gas composition, particularly the oxygen content, on the competition between the reduction and oxidation processes will be discussed.

DISSOCIATION ENERGY LIMIT

The intent in using a non-thermal plasma is to selectively transfer the input electrical energy to the electrons. An ideal situation would be where the kinetic energy of the electrons is dissipated entirely in the dissociation of NO molecules. The energy required to dissociate an NO molecule is 6.5 eV. This corresponds to the dissociation of 40 ppm of NO per Joule/liter of input energy density, as shown in Figure 1. The input energy density is the power deposited into the gas divided by the gas flow rate. For example, assuming a 100 kW engine puts out 500 ppm of NO at an exhaust flow rate of 1.5 liters per second per kW, then the minimum power needed by the plasma to dissociate all the NO would be about 2 kW.

Because of the relatively low concentration of NO in the exhaust gas, direct dissociation of NO by the electrons is not probable. The kinetic energy of the electrons is deposited primarily into the major exhaust gas components, N_2 and O_2. The electrons could lose considerable energy through reactions, such as the vibrational excitation of N_2, which do not promote the dissociation of NO.

RADICAL PRODUCTION LIMIT

The most useful deposition of electron kinetic energy into N_2 and O_2 is associated with the production of N and O radicals through electron-impact dissociation:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S) \qquad (1a)$$

$$e + N_2 \rightarrow e + N(^4S) + N(^2D) \qquad (1b)$$

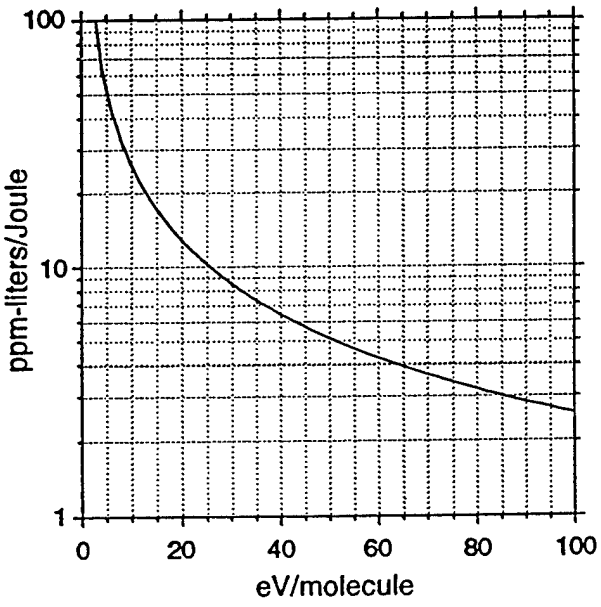

Figure 1. Conversion from "eV per molecule" to "ppm-liters per Joule".

$$e + O_2 \rightarrow e + O(^3P) + O(^3P) \qquad (2a)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^1D) \qquad (2b)$$

where $N(^4S)$ and $N(^2D)$ are ground-state and metastable excited-state nitrogen atoms, respectively, and $O(^3P)$ and $O(^1D)$ are ground-state and metastable excited-state oxygen atoms, respectively.

For now let us suppose that the plasma is not producing oxidative radicals. Let us further assume that all nitrogen atoms (labeled simply as N) can be used entirely for the reduction of NO:

$$N + NO \rightarrow N_2 + O \qquad (3)$$

In this case the energy required to reduce NO is simply determined by the energy required to produce N from the electron-impact dissociation of N_2. What is the energy required to implement this reduction scheme?

Figure 2 shows the G-value for electron-impact dissociation of N_2. The G-value is defined as the number of reactions per 100 eV of input electrical energy. The G-value depends on the average kinetic energy (mean energy) of the electrons in the plasma. In turn, the electron mean energy depends on the electric field that can be imposed on the plasma. Higher electric fields will accelerate the electrons to higher kinetic energies.

The highest electric field that can be applied while still maintaining a non-thermal plasma is known as the electrical breakdown threshold. Under atmospheric-

pressure conditions, the electrical breakdown threshold in an N_2 or air discharge plasma corresponds to an electron mean energy of around 4 eV. This corresponds to the consumption of 240 eV of electrical energy per N atom produced. The reader is referred to Ref. [3] for experimental verification of these statements.

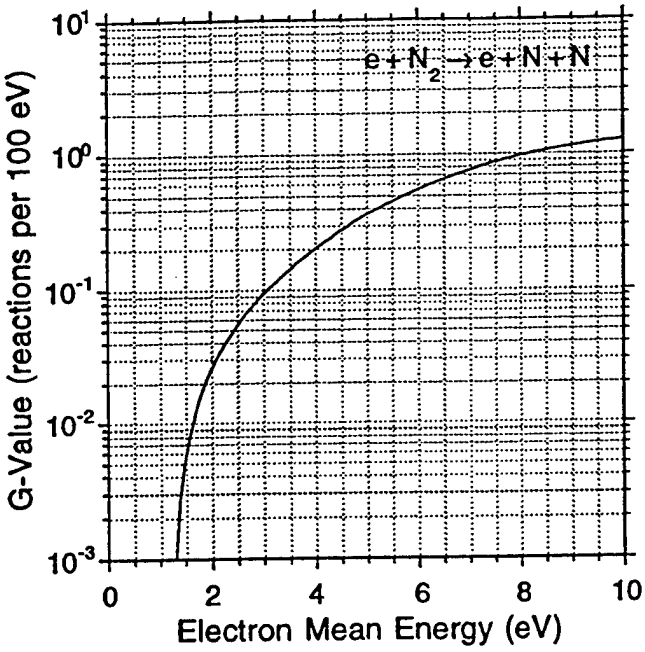

Figure 2. G-value for electron-impact dissociation of N_2 as a function of the average kinetic energy of the electrons in the plasma. The G-value is defined as the number of reactions per 100 eV of input electrical energy.

There are several proposals on how the electrical breakdown limit can be increased. For the sake of establishing a fundamental limit, let us assume that a very high electrical breakdown threshold can be achieved in practice. For a very high electron mean energy (> 10 eV), the G-value is around 1.25 N_2 dissociation reactions per 100 eV of input electrical energy. This corresponds to the consumption of 40 eV of electrical energy per N atom produced. This is the minimum energy required to produce an N atom even under the most ideal plasma condition. This condition can be achieved when very high kinetic energy electrons are injected into the gas stream, as verified experimentally in Ref. [4]. Based on reaction (3), the electrical energy required to reduce an NO molecule is 40 eV. This corresponds to the reduction of 6.5 ppm of NO per Joule/liter of input electrical energy density. Using the same example assuming a 100 kW engine putting out 500 ppm of NO at an exhaust flow rate of 1.5 liters per second per kW, the minimum power needed by the plasma to reduce all the NO would be greater than 10 kW.

EFFECT OF OXYGEN

There are several problems associated with the presence of O_2. These are:

(a) The dissociation energy of O_2 is smaller than that of N_2. The dissociation of O_2 will produce only oxidative radicals. With O_2 concentrations of 5% or more, a significant fraction of the input electrical power is dissipated in the dissociation of O_2. The ground state oxygen atoms, $O(^3P)$, convert NO to NO_2:

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad (4)$$

(b) The creation of metastable atomic nitrogen, particulary $N(^2D)$, can enhance undesired reactions in the presence of O_2. Rather than reducing NO, the $N(^2D)$ species would react with O_2 to produce NO:

$$N(^2D) + O_2 \rightarrow NO + O \qquad (5)$$

(c) The metastable atomic oxygen, $O(^1D)$, reacts with H_2O to produce OH radicals. The OH radicals convert NO and NO_2 to nitrous acid and nitric acid, respectively.

Figure 3 shows the N and O radical production efficiencies (number of radicals produced per 100 eV of electrical energy input) as functions of the average kinetic energy of the electrons in a plasma for a gas mixture consisting of 10%O_2, 10% CO_2, 5% H_2O and balance N_2.

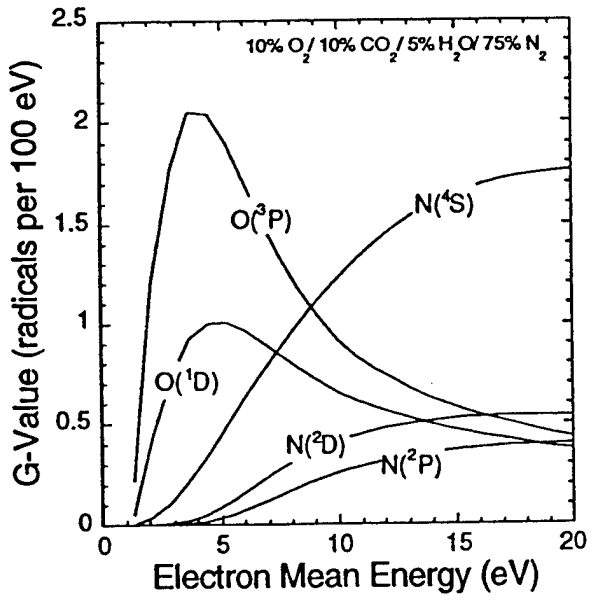

Figure 3. G-values for N and O radical production as a function of the average kinetic energy of the electrons in the plasma for a gas mixture consisting of 10%O_2, 10% CO_2, 5% H_2O and balance N_2. The G-value here is defined as the number of radicals produced per 100 eV of input electrical energy.

Because of the electrical breakdown limit, most non-thermal plasma reactors operate in a regime where the average kinetic energy of the electrons is in the 3 - 6 eV range. This is why non-thermal plasma reactors are very good at producing ozone. Unfortunately, the conditions for producing ozone are not the same conditions optimum for reducing NO_x.

High electron mean energies are required to optimize the production of $N(^4S)$, which is the only plasma species that can chemically reduce NO. However, at high electron mean energies, a large number of excited nitrogen atoms, $N(^2D)$ and $N(^2P)$, is produced during electron-impact dissociation of N_2. The excited nitrogen atom, $N(^2P)$, is rapidly converted to the metastable nitrogen atom $N(^2D)$. Because of the large rate constant for reaction (5) and the large concentration of O_2 relative to NO, the $N(^2D)$ species preferentially reacts with O_2 to produce NO. A large fraction of the $N(^4S)$ is consumed in reducing the NO that is produced by $N(^2D)$. This means that even under conditions where the electron kinetic energy is optimum for the dissociation of N_2, the presence of O_2 will make the minimum electrical energy for NO reduction greater than 40 eV per NO molecule. This corresponds to the reduction of less than 6.5 ppm of NO per Joule/liter of input electrical energy density.

CONCLUSION

In the absence of heterogeneous reactions, the reduction of NO in a plasma occurs by reaction with atomic nitrogen. Very high electron kinetic energies are required to optimize the production of atomic nitrogen from electron-impact dissociation of N_2. When the electron kinetic energy is optimum for N_2 dissociation, a large fraction of the atomic nitrogen produced is in the excited state. In the presence of O_2, the electrical energy requirement increases because of NO production by the excited atomic nitrogen species. Furthermore, the dissociation of O_2 promotes the oxidation of NO to NO_2 and nitric acid. Under the best plasma conditions, the minimum electricity requirement for true chemical reduction corresponds to the reduction of around 6.5 ppm of NO per Joule/liter of input electrical energy density.

ACKNOWLEDGMENT

The work was performed at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the Office of Energy Research and a Cooperative Research and Development Agreement with Cummins Engine Company.

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